OXYGEN VACANCY ORDERING IN YBa$_2$Cu$_3$O$_{7-y}$

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First principles total energy calculations have been performed for YBa$_2$Cu$_3$O$_x$ with x varying from 6.0 to 7.5. The results of these calculations have been used to determine the effective pair interactions for the oxygen ordering in the basal plane. The phase diagram calculated with these "first principles" pair interactions is in very good agreement with experiment. Comparison of the total energies for the O$_8$, O$_{8.5}$ and O$_7$ structures shows that the double-cell phase is thermodynamically stable.

The problem of oxygen ordering in the basal plane of YBa$_2$Cu$_3$O$_{7-y}$ is an important one which has received a great deal of attention recently. Experimentally[1], it is clear that the tetragonal to orthorhombic structural transition is associated with an ordering of the oxygen atoms into Cu-O chains. Theoretically, de Fontaine, Wille and co-workers[2] have proposed a simple Ising like model to describe the interactions between the oxygen atoms and have shown that, for a particular range of parameters, their model gives rise to a phase diagram in qualitative agreement with experiment. In contrast to this method which is based on localized effective pair interactions, Khachaturyan and Morris[3] have suggested an alternative approach where long range interactions produce the observed ordering. They conclude that the double-cell phase of YBa$_2$Cu$_3$O$_{8.5}$, with parallel Cu-O chains running through every second copper atom in the basal plane, is thermodynamically unstable, in disagreement with the conclusions of de Fontaine et al.

One way to resolve this controversy is to calculate the total energies of the structures using a first principles electronic structure method and see if the double-cell phase is higher or lower in energy than the average of the O$_8$ and O$_7$ phases. We have performed these calculations using the LMTO method[4]. The double cell phase was found to be more stable by 4.6mRy/O atom in the basal plane, and will clearly not decompose into a mixed O$_6$/O$_7$ phase.

The model proposed by de Fontaine et al[2,5] is an Ising like model with nearest and next nearest neighbor interactions. There are two different next nearest sites in the basal plane, one joined by a Cu atom, the other with no intervening atoms, so it is assumed that these two interactions are different, giving rise to an asymmetric next nearest neighbor Ising model described by three interactions: V$_1$, the nearest neighbor interaction, V$_2$, the second-neighbor interaction mediated by the Cu atom and V$_3$, the second-neighbor interaction with no intervening atoms. Wille et al[2] have shown that for an appropriate choice of parameters, this model can produce a phase diagram in qualitative agreement with experiment. The choice of parameters is very important, since the phase diagram can be qualitatively altered by choosing different values.

We have calculated these parameters from first principles by computing the total energies

for a number of different structures and using the Connolly Williams[6] method to extract the interaction energies. Care must be taken in deriving these parameters from the electronic structure calculations, since the total energies are of order thousands of Rydbergs, while the interaction parameters are only a few mRy. The following values were obtained:

$$V_1 = 6.9 \text{ mRy} \qquad V_2 = -2.4 \text{ mRy}$$
$$V_3 = 1.1 \text{mRy}$$

The phase diagram in figure 1 has been calculated from these parameters using the cluster variation method[7]. Agreement with experiment for the orthorhombic to tetragonal transition is excellent, considering that this is a first principles calculation with no fitting to experiment. The double-cell phase, labelled Ortho II, is clearly seen around $O_{6.5}$. The stability of this phase can be readily
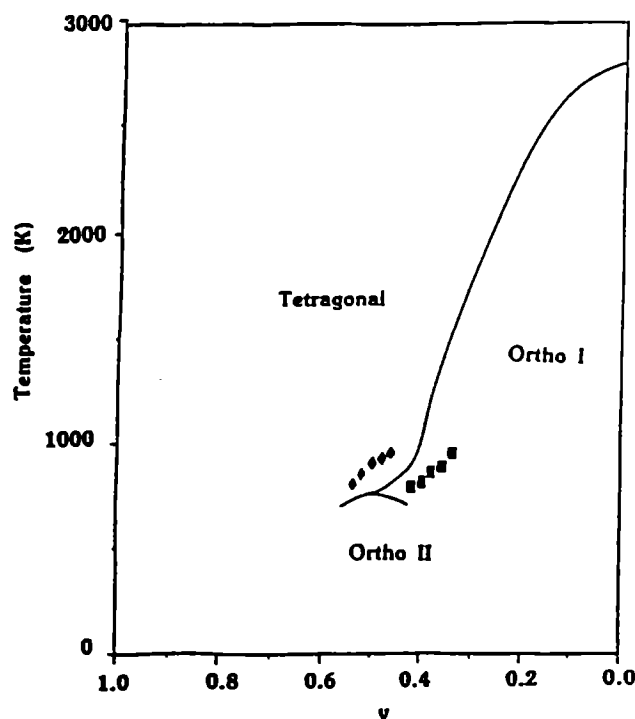
understood in terms of the calculated parameters: the negative V_2 term indicates that it is energetically favorable to form Cu-O chains (or, equivalently, Cu-vacancy ($\square$) chains), as seen in both $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_{6.5}$. The repulsive V_3 term suggests that the system would favor a state where the O-O and $\square$-$\square$ repulsive interactions are minimized, which is the case for the double cell phase.

FIGURE 1

Phase diagram for $YBa_2Cu_3O_{7-y}$ calculated from the pair interactions derived from the total energy calculations. The diamonds[8] and squares[9] are experimental data points.

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